

# Soot volume fraction measurements over laminar pool flames of biofuels, diesel and blends

B. Tian<sup>a</sup>, C. T. Chong<sup>b</sup>, L. Fan<sup>a</sup>, J.-H. Ng<sup>c</sup>, C. Zhang<sup>a</sup>, S. Hochgreb<sup>a</sup>

<sup>a</sup>*Department of Engineering, University of Cambridge, Trumpington Street, CB2 1PZ  
Cambridge, UK*

<sup>b</sup>*UTM Centre for Low Carbon Transport in cooperation with Imperial College London,  
Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia*

<sup>c</sup>*Faculty of Engineering and the Environment, University of Southampton Malaysia  
Campus (USMC), 79200 Iskandar Puteri, Johor, Malaysia*

---

## Abstract

Biodiesel and blends with petroleum diesel have shown their potential as renewable alternative fuels for engines, with additional benefits of low particulate matter and low sulfate emissions. In this paper we measure the soot volume fraction produced by three different methyl esters processed biodiesels (extracted from palm (PME), soy (SME) and coconut (CME)), and their blends with petroleum diesel, in a series of co-flow stabilized laminar pool flames, using laser induced-incandescence (LII) and laser extinction optical methods. The soot volume fraction measurement results show that all neat biodiesels produce only up to 33% of the total soot volume compared to pure diesel, and that the total soot volume correlates directly with the degree of unsaturation of the biodiesels. Blending leads to approximately linear behaviour of total soot volume, with a shift in slope with smaller sensitivity towards neat diesel.

---

*Email address:* [bt312@cam.ac.uk](mailto:bt312@cam.ac.uk) (B. Tian )

*Keywords:* Biodiesel, Soot, Laser induced incandescence, Laser extinction

---

## 1. Introduction

1 A variety of industrially processed bioderived fuels have been introduced  
2 as replacements for diesel fuel, such as palm, rapeseed, coconut and soy.  
3 These are processed and tailored as a replacement for diesel, with suitably  
4 low cetane numbers, and viscosities adjusted as additives for appropriate  
5 operation in existing engines. These replacement fuels typically have 10-  
6 15% oxygen as elemental composition, which offers an additional benefit in  
7 the form of lower soot emissions, with some variations on the effect on  $\text{NO}_x$   
8 [1]. A typical biodiesel consists of a mixture of monoalkyl esters of long-chain  
9 methyl esters produced via the transesterification process, in which the triglyc-  
10 erides contained in vegetable oils and animal fats react with methanol to form  
11 methyl esters and glycerol [2]. The chemical oxidation and soot formation  
12 pathways of biodiesel have been investigated in a number of studies [3, 4].  
13 Although many studies have been produced in engines, fewer measurements  
14 have been made in well controlled devices suitable for model comparisons,  
15 such as vaporised laminar co-flow diffusion flames [5, 6], counterflow diffusion  
16 flames [7], spray flames [8], high pressure injection constant volume combus-  
17 tion chambers [9, 10] and wick-fed lamp diffusion flames [11]. Nerva *et al.*  
18 [10] studied the soot formation of soy biodiesel using soot extinction, laser  
19 induced incandescence (LII) and luminosity at pressures up to 6.7 MPa and  
20 1000 K. The soot concentration for biodiesel was found to be lower by an  
21 order of magnitude compared to diesel, highlighting the role of oxygen and  
22 molecular structure of biodiesel in reducing sooting propensity. In a similar

23 but separate study [9], soy biodiesel was found to yield a higher value of soot  
24 mass fractions compared to butanol. Unlike diesel, butanol is a relatively  
25 short alcohol chain dthat shows low sooting propensity. The effect of oxygen  
26 concentration in the vessel was also investigated. The flame luminosity and  
27 soot production were shown to decrease with decreasing oxidizer content in  
28 the mixture, whereas higher ambient temperatures in the chamber increased  
29 soot production. The propensity of sooting for model biodiesels has been  
30 studied by Feng *et al.* [7] in a non-premixed counter-flow flame configura-  
31 tion using biodiesel surrogates, in the form of fatty acid esters. The model  
32 biodiesel fuels were shown to produce significantly lower soot levels compared  
33 to the corresponding n-alkanes with similar carbon number. Interestingly,  
34 unsaturated methyl ester (methyl-crotonate:  $C_5H_8O_2$ ) was shown to exhibit  
35 higher sooting propensity compared to the corresponding saturated methyl  
36 ester (methyl-butanoate:  $C_5H_{10}O_2$ ), indicating that the effect of the unsat-  
37 uration level in biodiesel on soot formation could be prominent. This is in  
38 agreement with results from an engine test operated using linseed biodiesel:  
39 this fuel with a higher unsaturation level emitted higher particulate matter  
40 and hydrocarbons compared to the less unsaturated palm biodiesel [12].

41 Kholgy *et al.* [5] measured the soot volume fraction of a biodiesel sur-  
42 rogate consisting of 50% n-decane/50% methyl-octanoate (as a surrogate  
43 for methyl oleate) in an co-flow diffusion flame, using the laser extinction  
44 method. The results were used as validation target for chemical kinetic  
45 models. Their computational study showed that the soot volume fraction  
46 and temperature profiles for the biodiesel surrogate are similar to that of n-  
47 decane, indicating a negligible effect of ester moiety on soot formation. The

48 result shows the low degree of unsaturation in biodiesel, rather than oxygen  
49 composition, may play the main role in lowering soot formation. Merchan-  
50 Merchan *et al.* [6] used a similar setup and measurement technique to inves-  
51 tigate the extent of soot formation in the case of soy and canola biodiesels.  
52 Both biodiesels exhibited similar flame temperatures and soot volume frac-  
53 tion profiles. Tran *et al.* [11] investigated the sooting behaviour of soy-  
54 bean biodiesel/diesel blends using LII over a wick-fed lamp, showing that  
55 the biodiesel produced significantly lower soot, and that the variation was  
56 proportional to the blended fraction. Finally, Tran *et al.* [13] considered the  
57 burning and emission characteristics of biodiesels over a pool fire, but no soot  
58 measurements were made.

59 The present study addresses the following needs: (a) to provide absolute  
60 measurements of soot volume fraction over a controlled laminar pool fire of a  
61 known fuel; (b) to contrast the formation of soot over a pool fire for a range  
62 of biofuels with different degrees of unsaturation and for a range of blending  
63 conditions with diesel fuel.

64 Extinction-calibrated LII has been proven to be a robust non-intrusive  
65 method for soot volume fraction ( $f_v$ ) measurement in flames [14–16]. How-  
66 ever, in high soot loading environments, LII suffers from significant signal  
67 trapping [17]. To tackle the problem, a deconvolution method was used in  
68 the present study to correct the 2D LII images and provide quantitative  
69 measurements for future studies.

## 70 2. Methodology

### 71 2.1. Experiment

72 Figure 1 shows the co-flow stabilized laminar pool burner used in the  
73 present study. The burner consists of a co-flow tube ( $D = 96.8$  mm), a  
74 stainless steel fuel cup ( $D = 20$  mm, depth = 20 mm, wall thickness = 2.5  
75 mm) and a holder for the cup. The dimensions of the cup and holder are  
76 shown in Fig. 1. A ceramic heating plate (CHP,  $D=24$  mm, 12V,  $\leq 240$  °C)  
77 is used underneath the pool to keep a constant temperature of the fuel around  
78 120 °C. A co-flow air of 18.2 cm/s is added around the fuel pool to reduce  
the flickering of the flame. The biodiesels tested in this work are methyl

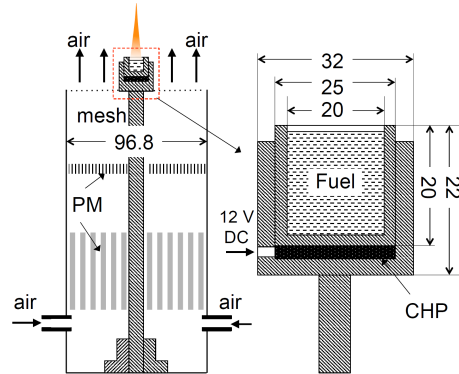


Figure 1: Co-flow stabilised laminar pool fire burner. CHP: ceramic heating plate; PM: porous material. Units in mm. Dimensions in mm, not to scale.

79

80 esters (ME) produced via a transesterification process from the feedstock  
81 of palm, soy and coconut oils, and are denoted as PME, SME and CME  
82 respectively. The composition of the biodiesels is measured using a standard  
83 Gas Chromatograph using a gas chromatograph (GC, Agilent 7620A) based  
84 on EN14103 standard, and listed in Table 2. The measured average formula  
85 of PME, SME and CME are:  $C_{18.1}H_{34.9}O_{2.0}$ ,  $C_{18.8}H_{34.5}O_{2.0}$  and  $C_{13.5}H_{26.9}O_{2.0}$ ,

86 respectively. All biofuels tested contain  $\geq 10\%$  (mass fraction) of oxygen, and  
 87 have a relatively low overall degree of unsaturation ( $\leq 1.51$ ), and are thus are  
 naturally expected to yield lower soot emissions. The behaviour of soot over

	PME	SME	CME
C8:0	0	0	6.78
C10:0	0	0	5.61
C12:0	0	0	51.00
C14:0	0.93	0	18.51
C16:0	39.85	11.62	9.26
C18:0	3.55	4.51	1.66
C18:1	43.14	23.03	6.06
C18:2	12.53	54.22	1.12
C18:3	0	6.62	0
Unsaturation	0.62	1.51	0.08
Avg. C chain	17.1	17.8	12.5
MW (g/mol)	284.3	291.5	221.2
$\Delta H$ (MJ/kg)	37.3	37.0	35.2
H	12.29	11.84	12.18
C	76.46	77.18	73.36
O	11.25	10.98	14.46

Table 1: Top section: Composition (mass percentage) of biodiesels measured using GCMS. C8:0 means the main chain of eight carbon atoms with zero C=C double bonds. Bottom section: Properties and elemental mass percentage of biodiesels. The degree of unsaturation is calculated by multiplying the mass fraction of each species times the associated number of C=C double bonds. Heat values  $\Delta H$  are from Ref. [18].

88

89 pool flames was investigated for a series of biodiesels and their blends with  
 90 petroleum diesel (D100). The blends are indicated by the initial of the biofuel  
 91 (P, S or C) and the percent by mass used in the mixture, *e.g.* P20 refers to  
 92 20% by mass in palm oil biodiesel. In all tests, the co-flow air flow velocity  
 93 is kept at 18.2 cm/s. The fuel consumption rate of each case is measured by  
 94 weighing the fuel burned over 10 min stable combustion, resulting in values

95 between 0.085-0.097 g/min.

96 The 2D LII measurements were performed using an similar set-up to that  
97 in Ref. [16]. The laser source is a 532 nm Nd:YAG laser (Litron nanoPIV)  
98 firing at 10-25 Hz. The laser beam is collimated into a parallel sheet by a  
99 series of beam shaping optics, followed by an aperture to generate a veri-  
100 fied top-hat profile. The LII signal induced by the laser sheet was captured  
101 by an ICCD camera (LaVision Nanostar  $1024 \times 1280$  pixels), fitted with  
102 a lens (Nikon AF Micro Nikkor 60 mm, f/5.6) and a band filter (Thorlabs  
103 FB400-40, central  $\lambda = 400 \pm 8$  nm, FWHM = 40 nm) which minimises the  
104 luminosity from PAH fluorescence,  $C_2$  and flame radiation. A delay of 20 ns  
105 was applied to the intensifier gate to avoid the interference of PAH LIF and  
106 residual laser scatter. A relatively short intensifier gate width of 30 ns was  
107 used to avoid bias towards larger particles [19]. The laser fluence used in the  
108 LII measurement was carefully selected. Figure 2 shows the dependence of  
109 the LII signal on the fluence of the laser sheet for the highest soot producing  
110 cases D100, P100, S100 and C100. The LII signal at each fluence represents  
111 the average value of 200 images at 20 Hz after background subtraction, ob-  
112 tained from the signal intensity between 0 to 35 mm height above the burner  
113 (HAB). The fuel pool surface is kept 1 mm below the cup lip before each mea-  
114 surement, and during the 10 second measurement, no significant decrease of  
115 the fuel surface level is observed as the fuel consumption rate is small ( $<0.1$   
116 g/min). All values are normalized using the maximum value of the case for  
117 purposes of locating the signal peak. In all cases, the LII signal rises rapidly  
118 with increasing laser fluence, as the temperature of the particles increase,  
119 reaching the sublimation point and an approximately fixed temperature and

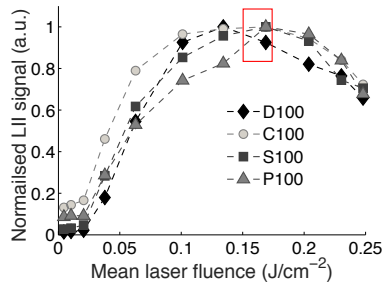


Figure 2: Fluence dependence of the LII signal for four unblended cases as a function of the fluence of laser sheet; the peak or plateau region (in the *marked rectangle*) is selected for the LII measurements. The values of LII signal intensities of each case are normalised using by maximum value for each fuel.

120 signal at a fluence around  $0.15 \text{ J/cm}^2$ , as indicated in the marked rectangle.  
 121 In this region, the LII signal is less sensitive to local laser fluence, which  
 122 allows a simplified description of the signal. In this work, we assume that  
 123 the fluence dependence of LII signal of all blended cases is similar to the pure  
 124 fuel cases, as their response curve should be somewhere in between the pure  
 fuel cases. Figure 3 shows the beam profile and variance averaged over 200

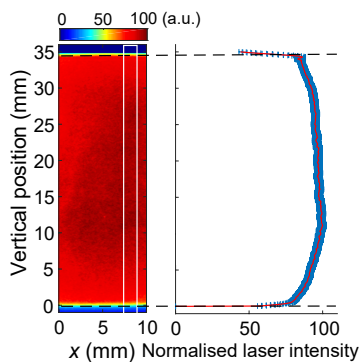


Figure 3: Normalised laser beam intensity profile used for LII excitation. Left: Rhodamine 6G fluorescence excited by laser sheet in a cuvette; right: integrated fluorescent light intensity profile over the region (red line) over the rectangle marked with a white border. Blue error bars indicate the signal variance shot-to-shot.

125

126 shots at 20 Hz, as characterised by the resulting fluorescence in a cuvette



127 containing Rhodamine 6G dye. The local intensity fluctuation of the laser  
 128 sheet as represented by the standard deviation is lower than 5%, and the  
 129 corresponding error introduced by fluctuations in spatial fluence is smaller  
 130 than 3%. All images are averaged after background noise subtraction. The  
 131 nominal spatial resolution is  $50 \mu\text{m}/\text{pixel}$  for an imaging area of  $35 \times 35 \text{ mm}^2$ .

## 132 2.2. LII calibration and correction

133 Laser extinction measurements are performed for a quantitative calibra-  
 134 tion of the LII signal [14]. A diode laser (Omicron LuxX-638-150, 638 nm  
 135 wavelength) is used as laser source for extinction. The laser beam intensity  
 136 ahead and behind soot absorption,  $I_0$  and  $I_t$ , respectively, are determined  
 137 using photodiodes (Thorlabs SM05PD1A Silicon Photodiode, 350-1100 nm).  
 138 The extinction ratio of the laser beam  $A = I_t/I_0$  can be expressed as [14, 16]:

$$A = \frac{I_t}{I_0} = \exp\left(-\int K_e dx\right) \quad (1)$$

139 where  $x$  is the path length across the sampling region, and  $K_e$  is the extinction  
 140 coefficient. The extinction coefficient  $K_e$  can be related to the local soot  
 141 volume fraction  $f_v$  in the Rayleigh regime (particle smaller than wavelength)  
 142 as:

$$K_e = \frac{6\pi E(m)}{\lambda_e} f_v \quad (2)$$

143 where  $E(m)$  is the absorption function of soot  $E(m) = -\text{Im}\left(\frac{m_e^2-1}{m_e^2+2}\right)$  and  $m_e$   
 144 is the complex refractive index of soot at the extinction wavelength  $\lambda_e$  (638  
 145 nm).

146 The local value of  $f_v$  can be determined in the axisymmetric system by  
 147 spatial differentiation of the total absorption factor  $A$ , which is a function

148 of chord distance  $x$ , obtained at the centreline of the flame via inverse Abel  
 149 transform [14, 16]:

$$f_v(r) = \frac{\lambda_e}{6\pi^2 E(m)} \int_x^\infty \frac{[\ln A(x)]'}{\sqrt{x^2 - r^2}} dr \quad (3)$$

150 where  $r$  is the radial distance. In the present study, the location HAB=25  
 151 mm in D100 flame is selected to conduct extinction measurements, as this  
 152 is close to the location of maximum integrated LII signal  $\int S_m dx$ . The  
 153  $f_v$  value is then calibrated from the measured LII signal intensity  $S_m$  by  
 154 assuming that the LII and extinction signals are linearly proportional (as  
 155 detailed in the following sections).

156 No reduction of LII signal is observed along the propagation direction of  
 157 the laser sheet, indicating the whole probe volume is in the plateau region of  
 158 LII measurement (Fig. 2), and a correction for the attenuation of the laser  
 159 sheet is considered unnecessary. However, because the flames in the present  
 160 study produce relatively high soot concentrations, the LII signal collected  
 161 is subject to trapping as it travels from the excitation plane to the camera,  
 162 and a correction on the signal trapping is necessary before the calibration  
 163 [17]. Since the flame is axisymmetric, the attenuation of the LII signal in  
 164 the flame due to signal trapping (as a function of  $x$ ) can be estimated from  
 165 the absorption ratio obtained for the extinction measurement along chord  
 166 distance  $x$ . In the present study, we measured  $A$  at HAB=25 mm for D100  
 167 along  $x$  over a step distance of 0.25 mm from  $x = -5$  mm to 5 mm, generating  
 168 a well-resolved  $A(x)$ . By combining Eqs. (1) and (2) and considering that  
 169 the LII absorption only occurs through one half of the symmetric flame, the

170 corrected LII signal  $S(x)$  can be obtained from the measured signal  $S_m(x)$ :

$$S(x) = S_m(x) A(x) \exp\left(-\frac{\lambda_e E(m_L)}{2\lambda_s E(m_e)}\right) = S_m K_c(x) \quad (4)$$

171 where  $K_c(x)$  is the correction constant;  $m_L$  and  $m_e$  are calculated at 400  
 172 nm and 638 nm, respectively, to account for the different absorption ratios  
 173 at the two wavelengths. Values of  $E(m)$  at the two wavelengths are taken  
 174 as 0.41 and 0.27, respectively, referred to the latest review in [20] using a  
 175 RDG-FA model corrected for internal multiple scattering effects. The LII  
 176 signal at HAB=25 mm in D100 flame can finally be calibrated using the  
 177 extinction data by considering that the integrated  $f_v$  across the centerline  
 178 chord at a certain HAB yields a total logarithmic attenuation. We assume  
 179 that the corrected LII signal  $S$  is proportional to the soot volume fraction  
 180 with a linear coefficient, such that  $S = C f_v$  [14, 16, 21], so that at the flame  
 181 centerline, we have:

$$\ln \frac{I_t}{I_0} = \frac{6\pi E(m_e)}{\lambda_e} \frac{1}{C} \int_{-\infty}^{+\infty} S(r) dr \quad (5)$$

182 The calibration constant  $C$  is therefore determined using Eq. (5), whose value  
 183 is  $2.9156 \times 10^8$  at HAB=25 mm in D100 flame. This value of  $C$  is assumed  
 184 to remain the same for all flames, since the soot produced by different liquid  
 185 fuels shares similar optical properties [22] and the imaging parameters are  
 186 kept unchanged throughout the experiment. A correction and calibration  
 187 method for all other cases is then possible, using the known value of  $C$ , with  
 188  $f_v$  as the only unknown variable, and one value of  $A$  for the chord centerline

189 at the same reference point. Considering the at a fixed chord position  $x$  at  
 190 in flame center,  $r = x$ ,  $S_m(x) = S_m(r)$ , we have:

$$Cf_v(r) = S_m(r) \exp \left( -\frac{12\pi E(m_L)}{\lambda_s} \int_0^{\infty} \frac{rf_v(r)}{\sqrt{r^2 - x^2}} dr \right) \quad (6)$$

191 The exponential factor represents the attenuation of the LII signal ex-  
 192 pressed in Eq. (4). By discretizing a cross section at a particular height of  
 193 the flame into a series of concentric rings, and numbering the values from  
 194  $i=0$  to  $N$ , the Eq. (6) can be written as:

$$Cf_v(i) = S_m(i) \exp \left( -\frac{6\pi E(m_L)}{\lambda_s} \sum_{j=i}^N f_v(j) \Delta_{i,j} \right) \quad (7)$$

195 where  $\Delta_{i,j}$  is given by Eq. (8) by assuming the distance between two adjacent  
 196 rings (pixels) is  $\delta$ :

$$\Delta_{i,j} = \begin{cases} \delta \left( \sqrt{j^2 - i^2} - \sqrt{(j-1)^2 - i^2} \right), & i < j \leq N \\ 0, & j \leq i \end{cases} \quad (8)$$

197 For  $i = N$ , the signal is emitted from the outermost ring, which is considered  
 198 as unattenuated:  $S(N) = S_m(N)$ , so we have  $f_v(N) = S_m(N)/C$ . For other  
 199 rings from  $i = N - 1$  to  $i = 1$ , as the term  $f_v(i)$  is the only unknown variable  
 200 in Eq. (7) and appears in both sides of the equation, and can therefore be  
 201 solved for iteratively in descending order from  $i = N - 1$  to  $i = 1$ .

202 **3. Results and discussion**

203 Both corrected and uncorrected  $f_v$  profiles at HAB=25 mm for the D100  
 204 flame are shown in Fig. 4 and compared with the extinction data. The value  
 205 of the correction constant  $K_c$  is obtained by extinction measurements in 0.25  
 206 mm steps along the radius (described in Section 2.2) and interpolated to  
 207 a resolution of 50  $\mu\text{m}$  to correct  $S_m$ . The data shows that signal trapping  
 208 causes about 14% underestimation of  $f_v$  at the flame center, and less than 5%  
 at the edges. Figure 5 shows the natural luminosity of all tested flames and

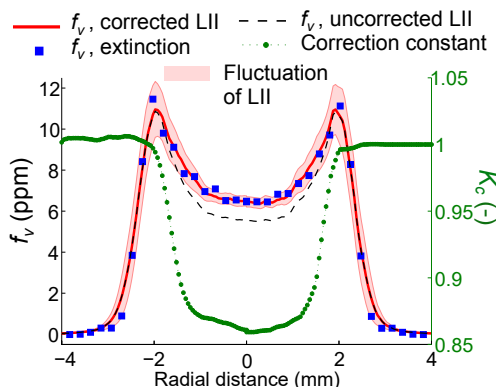


Figure 4: Corrected (red line with pink shaded fluctuation region) and uncorrected (dashed line)  $f_v$  profile at HAB=25 mm of D100 flame, compared to values obtained from extinction  $f_v$  (blue squares), and correction coefficient  $K_c$  (green dots).  $K_c$  is obtained by moving the extinction measurement in 0.25 mm steps and interpolated to the resolution of 50  $\mu\text{m}$ .

209

210 the corresponding  $f_v$  map from HAB=0 to 35 mm. The fuel consumption  
 211 rate for each case is noted on each flame photo. The fuel consumption rate is  
 212 within 7% for all 16 cases, but the visible flame heights are widely different,  
 213 from 25 mm to more than 80 mm (sooting flames). All pure biodiesel visible  
 214 flame heights are similar, and shortest in height, increasing approximately  
 215 linearly towards the highest visible heights of the pure diesel. In the latter

216 case (D100), the flame emits visible unburned soot from the flame tip, so  
 217 the flame height is not very well defined, as is the case for 20% and 40%  
 218 addition of all three biodiesels. Beyond 60% biofuel fraction or more, the  
 219 flames no longer emit soot, which means that any soot produced is oxidized  
 220 within the flame. The  $f_v$  maps for all cases are shown in Fig. 5 (rows 2  
 221 and 4). An obvious decrease in  $f_v$  with biodiesel addition can be observed in  
 222 all three series of flames, which is consistent with the expectation of oxygen  
 223 containing biodiesels [18]. The underlying data is reported as supplemental  
 material (Fig. S1) for ease of use by models. The spatial profiles of  $f_v$  at

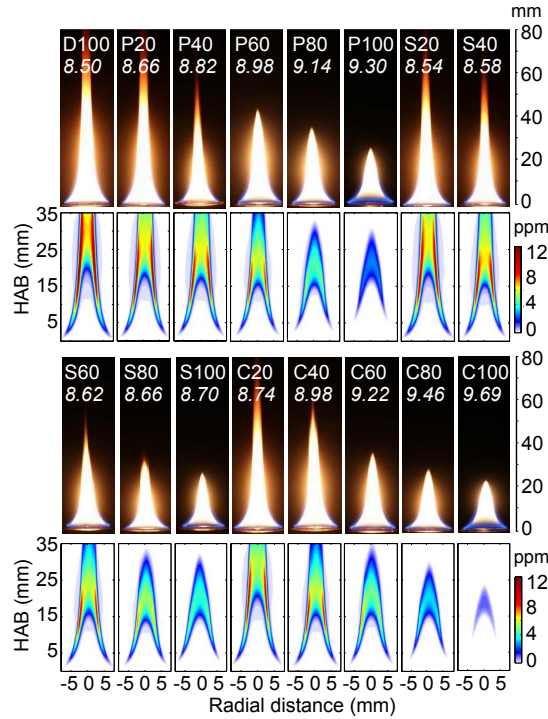


Figure 5: Natural luminosity of tested flames and corresponding  $f_v$  map from HAB=0 to 35 mm. The fuel consumption rate of each case is noted on each subfigure in units of  $10^{-2}$  g/min.

224

225 HAB=25 mm for all cases are compared in Fig. 6. The profile of D100

226 is plotted using red dashed lines in each sub-figure as a reference. At a  
227 particular height, the values of  $f_v$  replicate a similar linear behavior as the  
228 maximum  $f_v$  against the blend ratio of biofuels. The profiles indicate that  
229 for cases with biodiesel ratios lower than 60%, at this particular height, the  
230 maximum  $f_v$  appears in the annular region, in contrast with cases with high  
231 biodiesel ratio (80% and 100%), where the maximum  $f_v$  appears along the  
232 flame centerline.

233 The appearance of soot depends on the residence time of the fuel within  
234 a fuel-rich region at high temperatures. The heating value of the three fuels  
235 are similar, and all about 15% percent lower than petroleum diesel [18]. The  
236 expected adiabatic temperatures for the different fuels are within 35 K based  
237 on the heating values and equilibrium calculations. In the case of D100, soot  
238 is promptly formed at high temperatures near the base of the flame after a  
239 short residence time, and continues as the heat is transferred towards the  
240 centerline of the flame. More soot results near the high temperatures at the  
241 edge than from the cooler centerline. In the case of the oxygenated biodiesels,  
242 the high temperatures at the base are insufficient to produce sufficient soot  
243 fractions over a short residence time. Only after sufficient residence time  
244 at high temperatures, away from oxidiser does the biodiesel pyrolysis create  
245 sufficient soot at the centerline. At higher HABs, after sufficient residence  
246 time at high temperatures all soot profiles converge to maxima at the cen-  
247 terline, as shown in Fig. 5. The maximum soot volume fraction for each case  
248 is shown in 7, as a function of biodiesel mass fraction. CME and all of its  
249 blends with petroleum diesel produces the least  $f_v$ , while SME produces the  
250 most, certainly beyond the 40% blending ratio. This observation is consis-

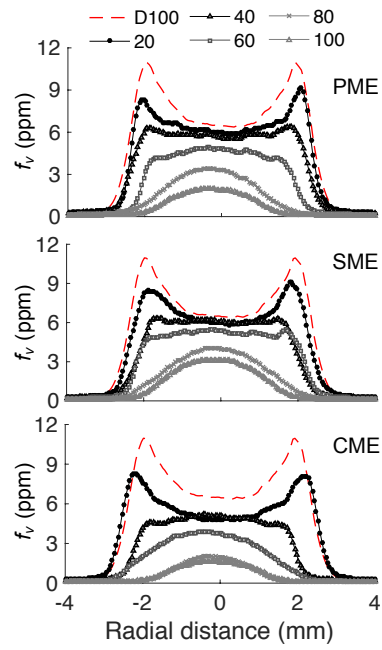


Figure 6: Profile of  $f_v$  at HAB=25 mm for three series of flames. D100 is plotted using red dashed lines in each sub-figure as reference.



251 tent with the fact that CME has the most saturated bonds in biodiesel (93%)  
 252 among the three tested fuels, compared with SME, whose saturated compo-  
 253 sition mass ratio is only about 16%. Over a blend ratio from 0 to 80%, the  
 254 maximum  $f_v$  is reduced by a factor of about 2.9 for CME, 2.2 for PME and  
 255 1.7 for SME, showing the addition of biodiesel can significantly suppress the  
 256 formation of soot. A parallel comparison among three biodiesels shows the  
 257 degree of unsaturation is a key factor for soot formation in tested flames. The  
 258 highly saturated CME (degree of unsaturation 0.08) produces only 22.4% of  
 259 maximum  $f_v$  compared with SME (degree of unsaturation 1.51) in pure form,  
 260 and in almost all blended cases. CME blend produces the least soot, while  
 261 SME produces the most. One exception to this trend happens when the mass  
 262 blend ratio is 20%, and the maximum  $f_v$  in P20 is slightly higher than that  
 263 of S20. This is yet not explained in the current research. The measurements  
 264 were repeated 3 times; the results are all very close to each other, with 2

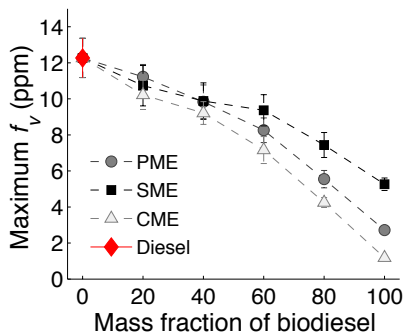


Figure 7: Maximum  $f_v$  as a function of biodiesel mass fraction.

265

266 comparison can be made by considering the soot flux in the axial direction,

267 which should scale as

$$\dot{V}_s = 2\pi \int r f_v u \, dr \quad (9)$$

268 where  $u$  is the mean axial velocity through the profile. The heating value of  
 269 all biofuels is similar, and about 10-15% lower than that of D100 [18], and  
 270 the fuel mass consumption rates are within 10%. Therefore it is reasonable  
 271 to assume that the value of  $u$  is not significantly different. In that case, the  
 272 total *relative* mean soot flux going into the flame region is represented by a  
 273 total area weighted soot volume fraction  $\bar{f}_v$ , as a function of height above  
 274 the burner, (Fig. 8). As expected, the mean soot volume fraction ranks in  
 275 a similar way as the maximum  $f_v$  plots. However, the mean value goes to  
 276 zero for the biofuels across the flame, the D100 (and the blends above 40%  
 biofuel, not shown) have a non-zero soot flux at the top of the image.

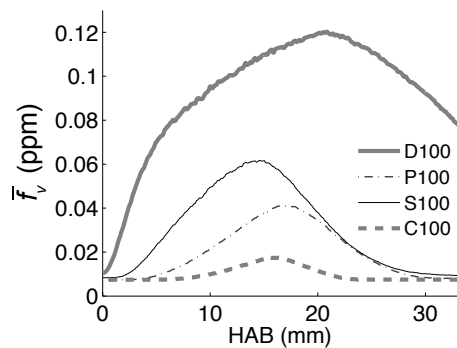


Figure 8: Normalised mean soot volume fraction  $\frac{1}{\pi R^2} \int_0^R 2\pi r f_v(r) dr$  in D100, P100, S100 and C100 flames, where  $R$  is the radius of the pool.

277

## 278 4. Conclusion

279 Extinction calibrated laser induced incandescence (LII) is applied to mea-  
 280 sure the soot volume fraction in laminar pool fires fueled with three different

281 biodiesels (PME, SME and CME) and their blends with petroleum diesel.  
282 The biodiesels have similar elemental composition but different degrees of  
283 unsaturation. The measured levels of maximum and total volume integrated  
284 over the image show that peak soot volume fractions produced by neat bio-  
285 fuels in this situation are 10.6 to 32.6% that of diesels, and that the fuel soot  
286 production ranks in order of degree of unsaturation. Blending leads to lower  
287 soot values, although the value is not linear across the entire range, with  
288 a slower reduction in total soot amount for blending of small quantities of  
289 biodiesel, followed by a faster decrease towards neat biofuel.

## 290 **Acknowledgements**

291 B. Tian is funded through a fellowship provided by ZEPI. C. Zhang is  
292 funded through a fellowship provided by CSC. The authors gratefully ac-  
293 knowledge the financial support from Universiti Teknologi Malaysia under  
294 grant number RG84263, and a Newton Advanced Fellowship (NA160115) for  
295 C. T. Chong.

## 296 **References**

- 297 [1] M. Lapuerta, O. Armas, J. Rodriguez-Fernandez, *Progress in Energy*  
298 *and Combustion Science* 34 (2008) 198 – 223.
- 299 [2] J. V. Gerpen, *Fuel Processing Technology* 86 (2005) 1097 – 1107.  
300 *Biodiesel Processing and Production*.
- 301 [3] O. Herbinet, W. J. Pitz, C. K. Westbrook, *Combustion and Flame* 154  
302 (2008) 507 – 528.

- 303 [4] J. P. Szybist, J. Song, M. Alam, A. L. Boehman, Fuel Processing Tech-  
304 nology 88 (2007) 679 – 691. Biofuels for Transportation.
- 305 [5] M. R. Kholghy, J. Weingarten, M. J. Thomson, Proceedings of the Com-  
306 bustion Institute 35 (2015) 905–912.
- 307 [6] W. Merchan-Merchan, S. McCollam, J. F. C. Pugliese, Fuel 156 (2015)  
308 129–141.
- 309 [7] Q. Feng, A. Jalali, A. M. Fincham, Y. L. Wang, T. T. Tsotsis, F. N.  
310 Egolfopoulos, Combustion and Flame 159 (2012) 1876–1893.
- 311 [8] C. Allouis, M. Romano, F. Beretta, L. Viegas, a. D’Alessio, Combustion  
312 Science and Technology 134 (1998) 457–475.
- 313 [9] H. Liu, C. F. F. Lee, M. Huo, M. Yao, Energy and Fuels 25 (2011)  
314 3192–3203.
- 315 [10] J.-G. Nerva, C. L. Genzale, S. Kook, J. M. García-Oliver, L. M. Pickett,  
316 International Journal of Engine Research 14 (2013) 373–390.
- 317 [11] M. K. Tran, D. Dunn-Rankin, T. K. Pham, Combustion and Flame 159  
318 (2012) 2181–2191.
- 319 [12] M. Salamanca, F. Mondragon, J. R. Agudelo, P. Benjumea, A. Santa-  
320 maria, Combustion and Flame 159 (2012) 1100–1108.
- 321 [13] V. Tran, C. Morton, R. N. Parthasarathy, S. R. Gollahalli, International  
322 Journal of Green Energy 11 (2014) 595–610.

- 323 [14] C. R. Shaddix, K. C. Smyth, *Combustion and Flame* 107 (1996) 418–  
324 452.
- 325 [15] H. A. Michelsen, C. Schulz, G. J. Smallwood, S. Will, *Progress in Energy*  
326 *and Combustion Science* 51 (2015) 2–48.
- 327 [16] B. Tian, Y. Gao, S. Balusamy, S. Hochgreb, *Applied Physics B* 120  
328 (2015) 469–487.
- 329 [17] F. Liu, K. a. Thomson, G. J. Smallwood, *Applied Physics B* 96 (2009)  
330 671–682.
- 331 [18] S. K. Hoekman, A. Broch, C. Robbins, E. Cenicerros, M. Natarajan,  
332 *Renewable and Sustainable Energy Reviews* 16 (2012) 143 – 169.
- 333 [19] E. Cenker, G. Bruneaux, T. Dreier, C. Schulz, *Applied Physics B* 118  
334 (2015) 169–183.
- 335 [20] A. Bescond, J. Yon, F. X. Ouf, C. Rozé, A. Coppalle, P. Parent, D. Ferry,  
336 C. Laffon, *Journal of Aerosol Science* 101 (2016) 118–132.
- 337 [21] F. Liu, G. J. Smallwood, *Applied Physics B* 112 (2013) 307–319.
- 338 [22] S. S. Krishnan, K.-C. Lin, G. M. Faeth, *Journal of Heat Transfer* 123  
339 (2001) 331.

340 **List of supplementary files**

341     Figure S1. Soot volume fraction  $f_V$  distribution (data-readable TIFF  
342 figure) in all tested cases.

343 **List of figure captions**

344 **Figure 1.** Co-flow stabilised laminar pool fire burner. CHP: ceramic heating  
345 plate; PM: porous material. Units in mm. Dimensions in mm, not to scale.

346 **Figure 2.** Fluence dependence of the LII signal for four unblended cases as  
347 a function of the fluence of laser sheet; the peak or plateau region (in the  
348 *marked rectangle*) is selected for the LII measurements. The values of LII  
349 signal intensities of each case are normalised using by maximum value for  
350 each fuel.

351 **Figure 3.** Normalised laser beam intensity profile used for LII excitation.  
352 Left: Rhodamine 6G fluorescence excited by laser sheet in a cuvette; right:  
353 integrated fluorescent light intensity profile over the region (red line) over the  
354 rectangle marked with a white border. Blue error bars indicate the signal  
355 variance shot-to-shot.

356 **Figure 4.** Corrected (red line with pink shaded fluctuation region) and un-  
357 corrected (dashed line)  $f_v$  profile at HAB=25 mm of D100 flame, compared  
358 to values obtained from extinction  $f_v$  (blue squares), and correction coeffi-  
359 cient  $K_c$  (green dots).  $K_c$  is obtained by moving the extinction measurement  
360 in 0.25 mm steps and interpolated to the resolution of 50  $\mu\text{m}$ .

361 **Figure 5.** Natural luminosity of tested flames and corresponding  $f_v$  map  
362 from HAB=0 to 35 mm. The fuel consumption rate of each case is noted on  
363 each subfigure in units of  $10^{-2}$  g/min.

364 **Figure 6.** Profile of  $f_v$  at HAB=25 mm for three series of flames. D100 is  
365 plotted using red dashed lines in each sub-figure as reference.

366 **Figure 7.** Maximum  $f_v$  as a function of biodiesel mass fraction.

367 **Figure 8.** Normalised mean soot volume fraction  $\frac{1}{\pi R^2} \int_0^R 2\pi r f_v(r) dr$  in

<sup>368</sup> D100, P100, S100 and C100 flames, where  $R$  is the radius of the pool.



	PME	SME	CME
C8:0	0	0	6.78
C10:0	0	0	5.61
C12:0	0	0	51.00
C14:0	0.93	0	18.51
C16:0	39.85	11.62	9.26
C18:0	3.55	4.51	1.66
C18:1	43.14	23.03	6.06
C18:2	12.53	54.22	1.12
C18:3	0	6.62	0
Unsaturation	0.62	1.51	0.08
Avg. C chain	17.1	17.8	12.5
MW (g/mol)	284.3	291.5	221.2
$\Delta H$ (MJ/kg)	37.3	37.0	35.2
H	12.29	11.84	12.18
C	76.46	77.18	73.36
O	11.25	10.98	14.46

Table 2: Top section: Composition (mass percentage) of biodiesels measured using GCMS. C8:0 means the main chain of eight carbon atoms with zero C=C double bonds. Bottom section: Properties and elemental mass percentage of biodiesels. The degree of unsaturation is calculated by multiplying the mass fraction of each species times the associated number of C=C double bonds. Heat values  $\Delta H$  are from Ref. [18].